Transient Glass Formation around a Quadrupolar Photoexcited Dye in a Strongly H-Bonding Liquid Observed by Transient 2D-IR Spectroscopy

Dereka, Bogdan ; Helbing, Jan ; Vauthey, Eric

Abstract: Intermolecular H-bonding dynamics around a photoexcited quadrupolar dye is directly observed using transient 2D-IR spectroscopy. Upon solvent-induced symmetry breaking, the H-bond accepting abilities of the two nitrile end-groups change drastically, and in extreme protic ('superprotic') solvents, a tight Hbond complex forms at one end. The time evolution of the 2D C N lineshape in methanol points to rapid, 2-3 ps, spectral diffusion due to fluctuations of the H-bonding network. Similar behaviour is observed in a superprotic solvent shortly after photoexcitation of the dye. However, at later time, the completely inhomogeneous band does not exhibit spectral diffusion for at least 5 ps, pointing to a glass-like environment around one side of the dye. About half of the excited dyes show this behaviour attributed to the tight H-bond complex, whereas the others are loosely bound. A weak cross peak indicates partial exchange between these excited state subpopulations.

DOI: https://doi.org/10.1002/anie.201808324

A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition Chemie

GDCh

www.angewandte.org

Accepted Article

Title: Transient Glass Formation around a Quadrupolar Photoexcited Dye in a Strongly H-Bonding Liquid Observed by Transient 2D-IR Spectroscopy

Authors: Bogdan Dereka, Jan Helbing, and Eric Vauthey

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201808324
Angew. Chem. 10.1002/ange.201808324

Link to VoR: http://dx.doi.org/10.1002/anie.201808324
http://dx.doi.org/10.1002/ange.201808324

WILEY-VCH

10.1002/anie.201808324

WILEY-VCH

Transient Glass Formation around a Quadrupolar Photoexcited Dye in a Strongly H-Bonding Liquid Observed by Transient 2D-IR Spectroscopy

Bogdan Dereka,[a] Jan Helbing,*[b,c] and Eric Vauthey,*[a,c]

Abstract: Intermolecular H-bonding dynamics around a photoexcited quadrupolar dye is directly observed using transient 2D-IR spectroscopy. Upon solvent-induced symmetry breaking, the H-bond accepting abilities of the two nitrile end-groups change drastically, and in extreme protic ('superprotic') solvents, a tight H-bond complex forms at one end. The time evolution of the 2D C≡N lineshape in methanol points to rapid, 2-3 ps, spectral diffusion due to fluctuations of the H-bonding network. Similar behaviour is observed in a superprotic solvent shortly after photoexcitation of the dye. However, at later time, the completely inhomogeneous band does not exhibit spectral diffusion for at least 5 ps, pointing to a glass-like environment around one side of the dye. About half of the excited dyes show this behaviour attributed to the tight H-bond complex, whereas the others are loosely bound. A weak cross peak indicates partial exchange between these excited state sub-populations.

Hydrogen-bonding interactions play key roles in many area of chemistry and govern the structure and dynamics of biological matter. In liquids, intermolecular H-bonds are highly dynamic, fluctuating and reorganizing within tens of femtoseconds to picoseconds.[1] This usually leads to a wide distribution of structures and to a strong broadening of the vibrational bands of solutes. 2D-IR spectroscopy has proven very powerful for getting insight into the H-bond dynamics of the solvation shell thanks to its ability to resolve inhomogeneous distributions and to trace vibrational frequencies with fs time resolution.[2] So far, however, most 2D-IR studies have focused on H-bond dynamics around solutes in the electronic ground state. While applying this technique to molecules in an electronic excited state is challenging, it is well known that H-bond strength can change significantly upon electronic excitation.[1a, 3] In this case, very different solvation dynamics can be anticipated.[4] Moreover, the few existing 2D-investigations of solvation in the excited state suggest that solvent motion around chromophores can be altered even in absence of specific H-bonding interactions.[5]

We investigated how the solvent dynamics around an excited chromophore change during the formation of a tight H-bond complex. We compared excited-state 2D-IR spectra of a quadrupolar molecule in solvents of different polarity and hydrogen-bonding strength. This molecule, **ADA** (Figure 1), has an A-π-D-π-A type motif, where A and D are electron accepting and donating groups. We observed dramatic changes in solvent dynamics around the excited solute, culminating in the transient formation of a glass-like environment in the most protic solvent.

ADA (2,5-bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2- *b*]pyrrole) consists of an electron-donating core with two symmetric acceptor branches and has no permanent dipole moment.[6] Its photoexcitation leads to the population of a symmetric quadrupolar excited state. However, in polar environments, solvent fluctuations break the symmetry, leading to an uneven distribution of the electronic density on the two cyano-capped ends.[7] As a consequence, in protic solvents, H-bond interactions between the solvent and the CN group located on the most excited side of ADA strengthen, whereas those at the other side weaken, amplifying symmetry breaking.[7a, 8]

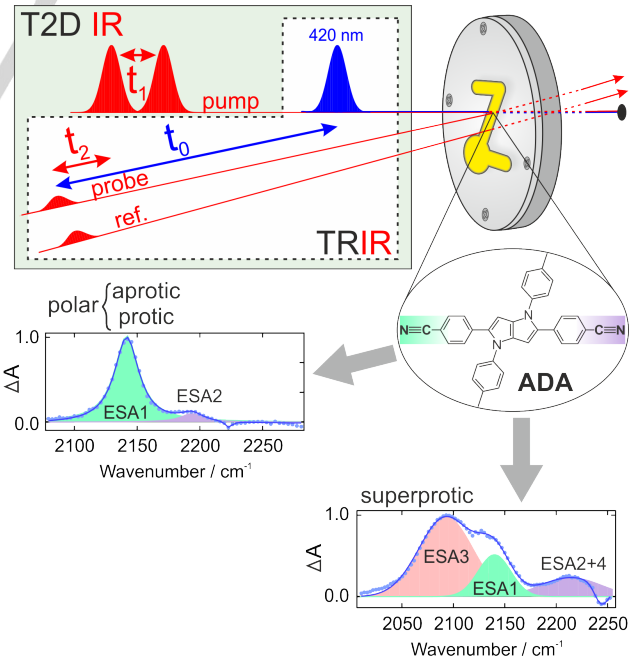


Figure 1. Schematic experimental pulse sequences: time-resolved infrared (TRIR) and transient 2D-IR (T2D-IR), structure of **ADA**, and representative TRIR spectra illustrating the ESA bands in the nitrile stretching region in polar/protic and in superprotic environments (as ESA4 is weaker than ESA2 and partially overlaps with this band, it cannot be clearly distinguished here).

[a] Dr. B. Dereka, Prof. E. Vauthey
Department of physical chemistry
University of Geneva
30, Quai Ernest Ansermet, CH-1211 Geneva, Switzerland
E-mail: eric.vauthey@unige.ch,
http://www.unige.ch/sciences/chifi/Vauthey/
[b] Dr. J. Helbing
Department of chemistry
University of Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
E-mail: jan.helbing@chem.uzh.ch,
http://www.chem.uzh.ch/en/research/groups/helbing.html
[c] Authors in alphabetic order.

Supporting information for this article is given via a link at the end of the document.

Spectroscopically, symmetry breaking gives rise to two distinct excited-state vibrational absorption (ESA) bands of the CN groups:[7c] an intense one, ESA1, and a weak one, ESA2, at higher frequency (Figure 1), with a splitting that increases with the degree of asymmetry. In strongly H-bonding liquids with a Kamlet-Taft parameter α>1.3 ('superprotic'), such as perfluorinated alcohols,[7a, 8] a tight solute-solvent complex forms on one side of **ADA**. This further localizes the excitation on one arm of the molecule and results in a two new bands, ESA3 and ESA4, with an even larger splitting than ESA1 and ESA2 (Figure 1).[7a, 7c] Dilution experiments revealed that, in the tightly H-bonded solute-solvent complex, **ADA** is also connected to the H-bond network of the surrounding solvent, through the directly bonded solvent molecule.[8]

The measurement of 2D-IR spectra of these ESA bands is enabled by the exceptionally large infrared absorption cross-section of the nitrile stretching vibrations of **ADA** in the excited state, which originates from the presence of the nearby $S_2 \leftarrow S_1$ electronic transition.[9] We used a time-domain variant[10] of the original set-up for transient 2D-IR (T2D-IR) spectroscopy,[11] as described in the Supporting Information. Briefly, electronic excitation of **ADA** was achieved with an actinic 420 nm femtosecond pulse. For the subsequent 2D-IR measurements, two collinear IR-pump pulses were used for the frequency-resolved excitation of the CN stretch vibrations of **ADA** in the S_1 state. The ensuing absorption changes were recorded after a time t_2 by an IR-probe pulse (**Figure 1**).

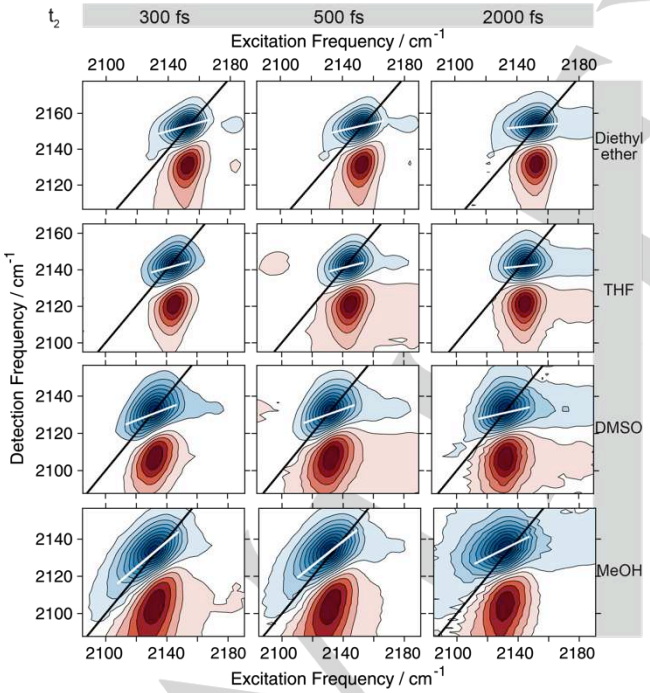


Figure 2. Normalized T2D-IR spectra in the ESA1 region in aprotic solvents of increasing polarity and in methanol, measured at t_0=40 ps after excitation of **ADA**.

Figure 2 shows T2D-IR spectra in the ESA1 region measured 40 ps after photoexcitation of **ADA** in aprotic solvents of varying polarity and in methanol. At this t_0 time, the S_1 state of **ADA** has equilibrated.[7a] The combined contributions of the ground-state bleach ($|1\rangle \leftarrow |0\rangle$ vibrational transition) and stimulated emission ($|1\rangle \rightarrow |0\rangle$) appear as negative signals on the diagonal (blue), whereas the induced $|2\rangle \leftarrow |1\rangle$ absorption is seen as a positive band at lower detection frequencies due to anharmonicity (red). The much weaker diagonal peak due to ESA2 lies outside the detection window of Figure 1, but weak coupling between ESA2 and ESA1 gives rise to small cross peaks at excitation frequencies near 2190 cm^{-1} already at the earliest t_2 times. The IR absorption cross-section of the CN stretching of **ADA** in the ground state is too small to give a measureable 2D-IR signal (see the weak dip in the TRIR spectra in Figure 1). Moreover, the frequency of the ground-state bleach at 2246 cm^{-1} coincides with that measured in the stationary absorption spectrum,[7a] indicating that the presence of the weak bleach does not lead to any significant distortion of ESA2.

Diagonal peaks in the 2D-IR spectra reveal the correlation between the excitation frequency and the frequency of the molecular response, and allow disentangling the homogeneous and inhomogeneous contributions to the vibrational linewidth.[2a] Already at the earliest t_2 times, the ESA1 bleach is narrow and largely circular in all aprotic solvents irrespective of their polarity, pointing to weak correlation and thus a largely homogeneous character of this band. Weak correlation is reflected by the small slope of the line joining the bleach minima (central line slope, CLS, Table S2),[12] shown in white in Figure 2.

The inhomogeneity is substantially larger in methanol (Table S1), indicating that hydrogen bonding to the CN groups leads to a broader distribution of instantaneous frequencies due to different H-bond strengths and lengths.[2c, 13] Within a few picoseconds, the CLS decays to zero due to spectral diffusion. Memory of the excitation frequency is lost as solvent molecules rearrange and sample all possible configurations (Figure 2). This dynamic picture of fluctuating H-bonds undergoing incessant rupture and formation is well-established for H-bonding liquids in the electronic ground state.[1d, 14]

However, a truly spectacular change in H-bond dynamics is observed in the superprotic hexafluoro-iso-propanol (HFP, Figure 3) in the ESA1/ESA3 region. The 2D band is much broader (note the larger spectral window relative to Figure 2) and, at the earliest t_2 time of 300 fs, it is completely inhomogeneous: the bleach signal is parallel to the diagonal with a CLS of unity, pointing to a significantly larger heterogeneity of H-bond strengths in HFP compared to conventional protic solvents like methanol. Furthermore, the data reveal a strong t_0-dependence of the temporal evolution of the 2D lineshape, i. e. the fluctuations of the H-bonding environment depend on the 'age' of the S_1 state of **ADA**. At t_0=8 ps, the spectrum is dominated by ESA1, which undergoes spectral diffusion and becomes circular within a few ps (Figure 3, second row). The t_2-dependence of the CLS can be reproduced by an exponential decay with a ~3.5 ps time constant (Figure 4), typical of solvent relaxation in HFP.[7a, 8] These dynamics are similar to those observed in methanol (Figure 3**,** third row), where the CLS decays in about 2 ps.

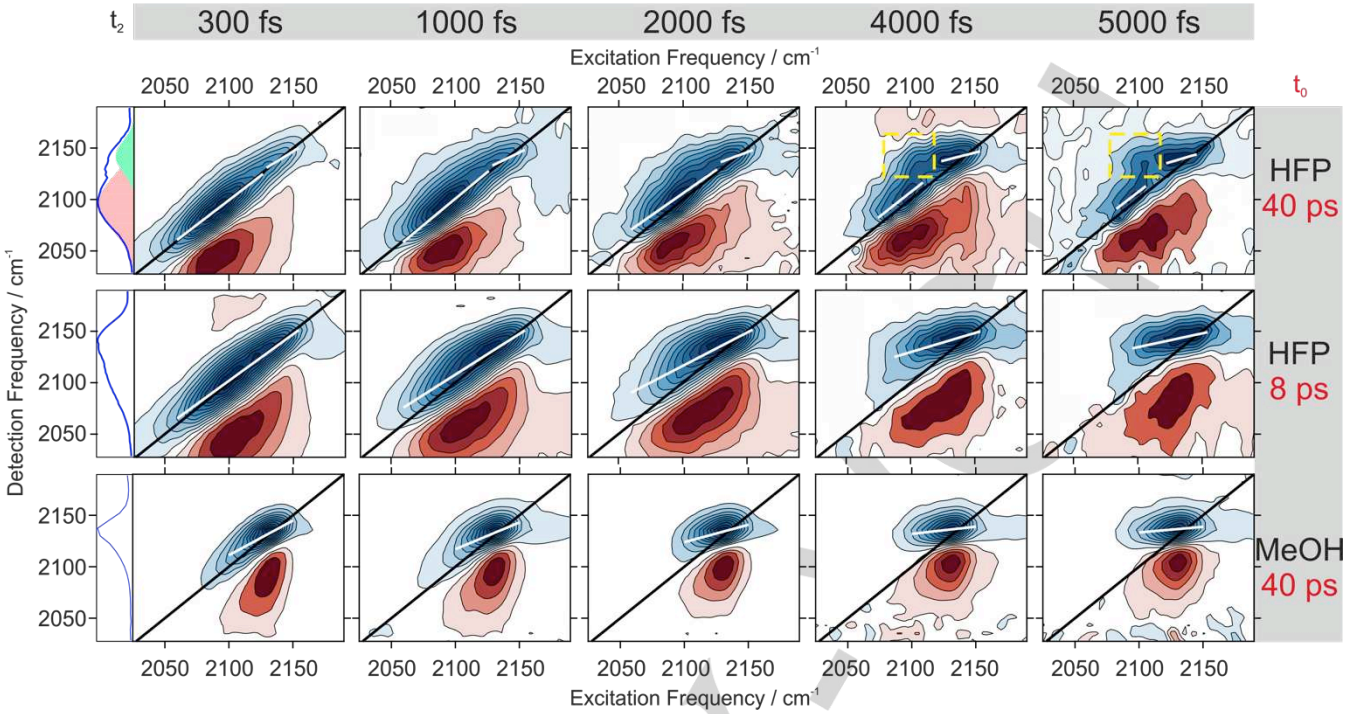


Figure 3. T2D-IR spectra in the ESA3/ESA1 region in the superprotic solvent HFP measured at t_0=8 and 40 ps after electronic excitation of **ADA**, and comparison with methanol (t_0=40 ps). Corresponding TRIR excited state absorption spectra are shown on the left.

The situation is completely different 40 ps after electronic excitation, when the additional ESA3 band of the tight complex has formed at the low-frequency side of ESA1. Spectral diffusion is now only observed for the residual ESA1, whereas ESA3 remains strongly inhomogeneous up to a t_2 time of at least 5 ps (Figure 3, first row), our detection limit corresponding to three vibrational lifetimes. The CLS of ESA3 remains close to unity at all accessible time delays (blue line in Figure 4). This absence of spectral diffusion indicates that the environment of the tight complex is static on the timescale of typical fluctuations of this solvent and resembles that of a glass.[15] Similarly slow spectral diffusion has only been reported for ionic liquids.[16] A substantial slowing down of the translational dynamics of water has also been observed in the solvation shell of different solutes.[17] Here, the glass-like behaviour is transient: it is not observed at early times (8 ps) after electronic excitation of **ADA**, but only when the tight complex is formed. By contrast, the spectral diffusion of ESA1, associated with the loosely-bonded **ADA** subpopulation, is only slightly slower than at t_0=8 ps (Figure 4). 2D-IR thus reveals that the similar width of ESA1 and ESA3 seen in TRIR is due to inhomogenous broadening, but associated with very different solvent dynamics. Unfortunately, the 2D-IR signal of ESA2 and 4, due to the CN group located on the other, less-polar side of **ADA**, is too weak and decays too rapidly to extract quantitative information (Figure S9).

The inhomogeneous broadening of ESA3 can be attributed to a distribution of H-bond strengths. The latter is due to the fact that **ADA** is connected to the H-bond network of the surrounding solvent via the tightly-bonded solvent molecule.[8] Moreover, the H-bond strength affects the degree of symmetry breaking of the excited state of **ADA**.[7a] Therefore, the broadening of ESA3 due to this distribution of H-bond strength is enhanced by the resulting distribution of the degree of symmetry breaking. The long persistence of this broadening thus strongly contrasts with the equilibrium behaviour of 'normal' H-bonding liquids like water, where the H-bond network, albeit altered by solutes, remains highly dynamic even in the presence of ions at high concentrations.[18] Likewise, the longest memory of inhomogeneity of the very strongly H-bonded excess proton in water,[19] was recently found to be only of the order of 200 fs.[20]

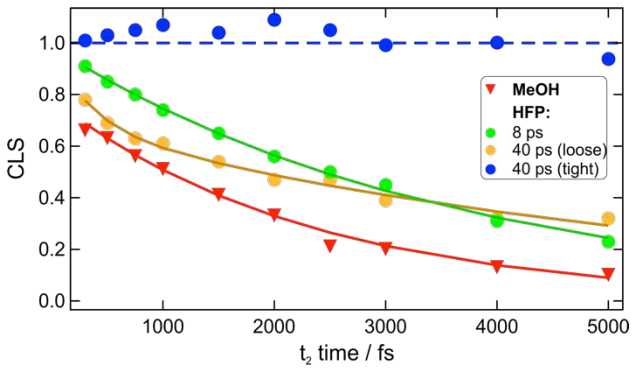
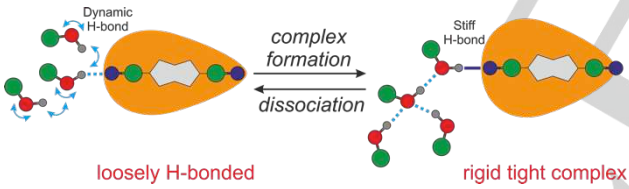


Figure 4. Time dependence of the central line slopes (CLS) of ESA1/ESA3 in HFP and methanol.

The two bands, ESA1 and ESA3, are associated with different sub-populations of **ADA** in the S_1 state, which are loosely and tightly H-bonded, respectively. Previous TRIR measurements revealed that both bands have the same 110 ps lifetime, whereas in solvents where no tight complexes are formed, ESA1 decays on a nanosecond timescale.[7a, 8] The shortening of the excited-state lifetime of **ADA** in HFP was attributed to the H-bond induced non-radiative deactivation (HBIND) mechanism,[8] whereas an equilibrium between the two sub-populations was invoked to account for the fact that both ESA1 and ESA3 share the same short lifetime (Figure S12).

If this equilibration takes place on a sufficiently short timescale, it should result in the appearance of an exchange cross peak between ESA1 and ESA3 in the 2D-IR spectra.[2b, 21] No such cross peak can be observed at short t_2 delays, but the 2D spectra recorded after 3-4 ps suggest the presence of a cross peak between ESA1 and the high-frequency side of ESA3 (yellow squares in Figure 3). Although its intensity is weak because the signal has substantially decayed (the excited-state lifetime of this vibration is <2 ps, Table S3), the cross peak does not have the full width of ESA3. This indicates that not all tight complexes participate in the exchange (at least within our 5 ps time window), but only those that contribute to the high-frequency side of ESA3, characterized by a weaker H-bond. One can anticipate that the most tightly-bound complexes are also in equilibrium with the loosely-bound subpopulation but on a significantly slower timescale than that accessible in the 2D experiment (Scheme 1). Indeed, the absence of spectral diffusion for ESA3 and a glass-like environment are not compatible with fast exchange between the tightly and loosely H-bonded sub-populations.



Scheme 1. Schematic illustration of the equilibrium between the loosely and tightly H-bonded **ADA** sub-populations (the orange area depict the symmetry-broken electronic distribution). For the sake of simplicity, the distribution of tight complex structures is omitted.

By comparing the ESA3/ESA1 band areas measured with the TRIR and 2D-IR techniques,[22] the sub-populations of tightly- and loosely-bound **ADA** molecules were estimated to be approximately equal in size after 40 ps, pointing to an equilibrium constant of K=1 and to similar free energies for both species (SI, Section S5). Most probably, the decrease of entropy upon glass formation around the tight complex compensates for the enthalpic factor due to the strengthening of the H-bond. In deuterated HFP, the equilibrium is significantly shifted toward the tight complex (K = 6.3) and the free energy of complex formation amounts to -4.5 kJ/mol. The difference with the protic HFP can be explained by a larger strength of deuterium bonds compared to hydrogen bonds in agreement with literature (Section S5).[23]

In summary, transient 2D-IR spectroscopy has provided unprecedented insight into H-bonding dynamics in an electronically excited state. It reveals the subtle interplay between intramolecular charge transfer, hydrogen-bond interactions and solvation. We monitored solvent motion around an excited quadrupolar molecule at different stages during the formation of a tight asymmetric H-bonded complex. Initially, the environment of the dye behaves as expected for a liquid causing normal spectral diffusion. However, upon complex-formation, it stiffens dramatically and behaves glass-like. No more spectral diffusion is observed on the typical timescale of solvent motion. This effect is most probably not limited to the quadrupolar **ADA** molecule investigated here. It can be expected to also occur with other dyes undergoing a subtantial increase of basicity upon photoexcitation in highly protic solvents capable of forming an H-bonding network.

Acknowledgements

The authors thank Prof. D. Gryko (Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw) for provision of the dye. This work was supported by the Swiss National Science Foundation (Project No. 200020-165890) and by the Universities of Geneva and Zurich.

Keywords: Hydrogen bonds • solvation dynamics • ultrafast spectroscopy • symmetry breaking • charge transfer

[1] a) E. T. J. Nibbering, T. Elsaesser, *Chem. Rev.* **2004**, *104*, 1887; b) F. Perakis, L. De Marco, A. Shalit, F. Tang, Z. R. Kann, T. D. Kühne, R. Torre, M. Bonn, Y. Nagata, *Chem. Rev.* **2016**, *116*, 7590-7607; c) S. T. Roberts, K. Ramasesha, A. Tokmakoff, *Acc. Chem. Res.* **2009**, *42*, 1239-1249; d) K. Shinokita, A. V. Cunha, T. L. C. Jansen, M. S. Pshenichnikov, *J. Chem. Phys.* **2015**, *142*, 212450; e) E. Salamatova, A. V. Cunha, K. Shinokita, T. I. C. Jansen, M. S. Pshenichnikov, *Phys. Chem. Chem. Phys.* **2017**, *19*, 27960-27967.

[2] a) P. Hamm, M. T. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy*, Cambridge University Press, Cambridge, **2011**; b) S. Woutersen, Y. Mu, G. Stock, P. Hamm, *Chem. Phys.* **2001**, *266*, 137-147; c) A. Ghosh, A. Remorino, M. J. Tucker, R. M. Hochstrasser, *Chem. Phys. Lett.* **2009**, *469*, 325-330; d) A. A. Bakulin, M. S. Pshenichnikov, H. J. Bakker, C. Petersen, *The Journal of Physical Chemistry A* **2011**, *115*, 1821-1829; e) J. Thøgersen, J. Réhault, M. Odelius, T. Ogden, N. K. Jena, S. J. K. Jensen, S. R. Keiding, J. Helbing, *J. Phys. Chem. B* **2013**, *117*, 3376-3388.

[3] a) G.-J. Zhao, K.-L. Han, *Acc. Chem. Res.* **2012**, *45*, 404-413; b) D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty, T. J. Meyer, *Chem. Rev.* **2012**, *112*, 4016-4093.

[4] a) C. F. Chapman, R. S. Fee, M. Maroncelli, *J. Phys. Chem.* **1995**, *99*, 4811-4819; b) J. L. Perez-Lustres, F. Rodriguez-Prieto, M. Mosquera, T. A. Senyushkina, N. P. Ernsting, S. A. Kovalenko, *J. Am. Chem. Soc.* **2007**, *129*, 5408-5418; c) M. Sajadi, M. Weinberger, H.-A. Wagenknecht, N. P. Ernsting, *Phys. Chem. Chem. Phys.* **2011**, *13*, 17768-17774; d) T. Kumpulainen, A. Rosspeintner, E. Vauthey, *Phys. Chem. Chem. Phys.* **2017**, *19*, 8815-8825.

[5] a) J. Bredenbeck, J. Helbing, P. Hamm, *Phys. Rev. Lett.* **2005**, *95*, 083201; b) L. M. Kiefer, J. T. King, K. J. Kubarych, *J. Phys. Chem. A* **2014**, *118*, 9853-9860.

[6] a) A. Janiga, E. Glodkowska-Mrowka, T. Stoklosa, D. T. Gryko, *Asian J. Org. Chem.* **2013**, *2*, 411-415; b) M. Krzeszewski, D. Gryko, D. T. Gryko, *Acc. Chem. Res.* **2017**, *50*, 2334-2345.

[7] a) B. Dereka, A. Rosspeintner, M. Krzeszewski, D. T. Gryko, E. Vauthey, *Angew. Chem. Int. Ed.* **2016**, *55*, 15624-15628; b) B. Dereka, M. Koch, E. Vauthey, *Acc. Chem. Res.* **2017**, *50*, 426-434; c) B. Dereka, E. Vauthey, *J. Phys. Chem. Lett.* **2017**, *8*, 3927-3932; d) B. Dereka, A. Rosspeintner, R. Stężycki, C. Ruckebusch, D. T. Gryko, E. Vauthey, *J. Phys. Chem. Lett.* **2017**, *8*, 6029–6034.

[8] B. Dereka, E. Vauthey, *Chem. Sci.* **2017**, *8*, 5057-5066.

[9] B. Dereka, A. Rosspeintner, Z. Li, R. Liska, E. Vauthey, *J. Am. Chem. Soc.* **2016**, *138*, 4643-4649.

[10] J. Helbing, P. Hamm, *J. Opt. Soc. Am. B* **2011**, *28*, 171-178.

[11] a) J. Bredenbeck, J. Helbing, R. Behrendt, C. Renner, L. Moroder, J. Wachtveitl, P. Hamm, *J. Phys. Chem. B* **2003**, *107*, 8654-8660; b) C. Kolano, J. Helbing, M. Kozinski, W. Sander, P. Hamm, *Nature* **2006**, *444*, 469.

[12] K. Kwak, S. Park, I. J. Finkelstein, M. D. Fayer, *J. Chem. Phys.* **2007**, *127*, 124503.

[13] M. Maj, C. Ahn, B. Błasiak, K. Kwak, H. Han, M. Cho, *J. Phys. Chem. B* **2016**, *120*, 10167-10180.

[14] a) M. Ji, M. Odelius, K. J. Gaffney, *Science* **2010**, *328*, 1003-1005; b) J. D. Eaves, J. J. Loparo, C. J. Fecko, S. T. Roberts, A. Tokmakoff, P. L. Geissler, *Proc. Natl. Acad. Sci.* **2005**, *102*, 13019.

[15] a) D. J. Hoffman, K. P. Sokolowsky, M. D. Fayer, *J. Chem. Phys.* **2017**, *146*, 124505; b) A. Shalit, F. Perakis, P. Hamm, *J. Phys. Chem. B* **2013**, *117*, 15512-15518.

[16] S. Dutta, Z. Ren, T. Brinzer, S. Garrett-Roe, *Phys. Chem. Chem. Phys.* **2015**, *17*, 26575-26579.

[17] G. Ramakrishnan, M. González-Jiménez, A. J. Lapthorn, K. Wynne, *J. Phys. Chem. Lett.* **2017**, *8*, 2964-2970.

[18] a) D. Laage, J. T. Hynes, *Proc. Natl. Acad. Sci.* **2007**, *104*, 11167-11172; b) Y.-S. Lin, B. M. Auer, J. L. Skinner, *J. Chem. Phys.* **2009**, *131*, 144511; c) S. T. van der Post, H. J. Bakker, *Phys. Chem. Chem. Phys.* **2012**, *14*, 6280; d) G. Stirnemann, E. Wernersson, P. Jungwirth, D. Laage, *J. Am. Chem. Soc.* **2013**, *135*, 11824-11831; e) S. A. Yamada, W. H. Thompson, M. D. Fayer, *J. Chem. Phys.* **2017**, *146*, 234501.

[19] F. Dahms, B. P. Fingerhut, E. T. J. Nibbering, E. Pines, T. Elsaesser, *Science* **2017**, *495*, 491-495.

[20] J. A. Fournier, W. B. Carpenter, N. H. C. Lewis, A. Tokmakoff, *Nat. Chem.* **2018**, *in press*, DOI: 10.1038/s41557-41018-40091-y.

[21] J. Zheng, K. Kwak, J. Asbury, X. Chen, I. R. Piletic, M. D. Fayer, *Science* **2005**, *309*, 1338-1343.

[22] P. M. Donaldson, P. Hamm, *Angew. Chem. Int. Ed.* **2013**, *52*, 634-638.

[23] a) S. Scheiner, M. Cuma, *J. Am. Chem. Soc.* **1996**, *118*, 1511-1521; b) R. A. Nicodemus, A. Tokmakoff, *Chem. Phys. Lett.* **2007**, *449*, 130-134.

10.1002/anie.201808324

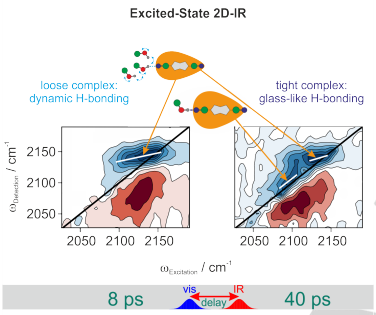
WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

A few picoseconds after its excitation, the quadrupolar dye studied here forms a tight and asymmetric hydrogen-bond complex with the solvent. Transient 2D-IR spectroscopy reveals that this results in a dramatic slowing down of the solvent dynamics around the dye. The surrounding solvent exhibits a glass-like behaviour.



B. Dereka, J. Helbing, E. Vauthey**

Page No. – Page No.

Transient Glass Formation around a Quadrupolar Photoexcited Dye in a Strongly H-Bonding Liquid Observed by Transient 2D-IR Spectroscopy